Environmental Transport and Fate of Alkylates

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Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California

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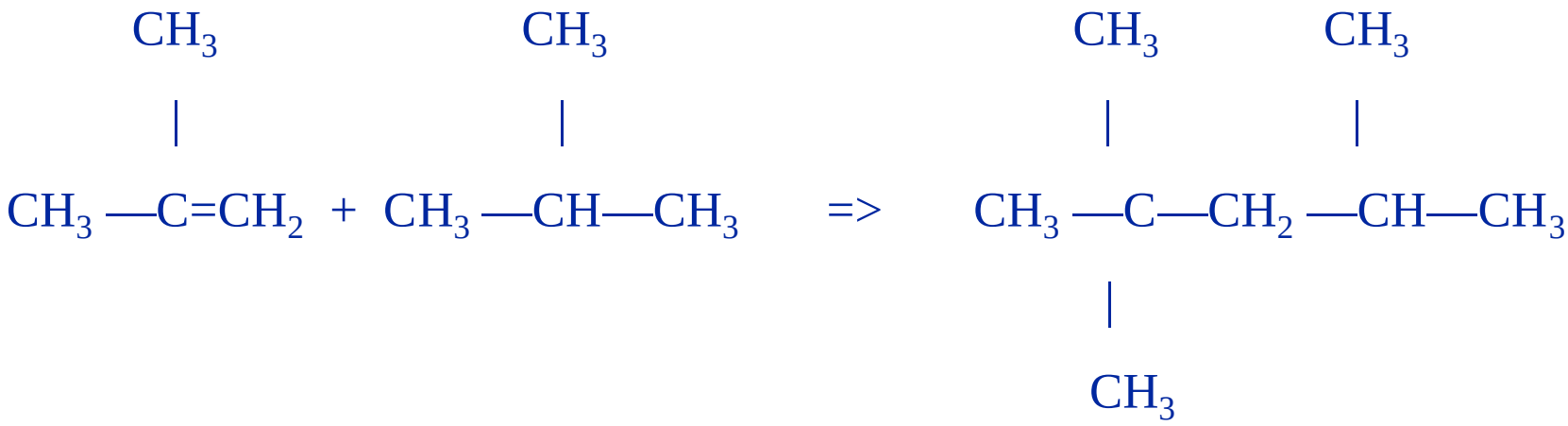
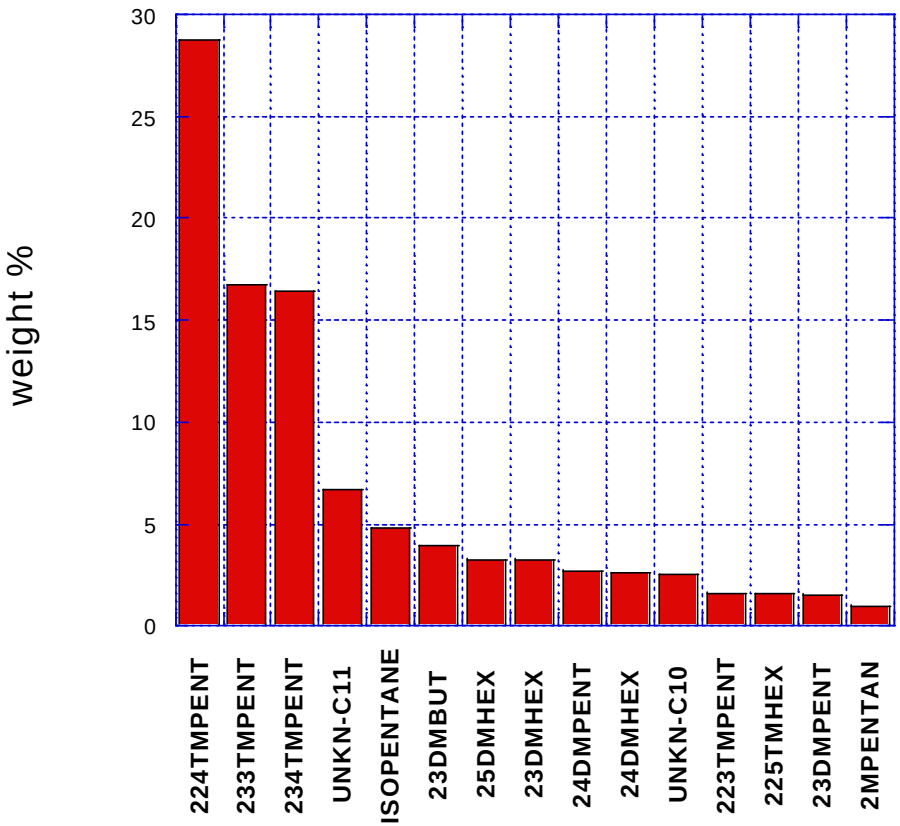
Alkylate synthesis: basic reaction



Isobutene (2-Methylpropene) + Isobutane (2-Methylpropane) => Isooctane (2,2,4-Trimethylpentane)

The reaction is catalyzed with sulfuric acid at low temperature< 10°C.

Alkylate composition



Data from STRATCO

Percentages are in agreement with those presented by Durett *et al.* for a finished alkylate (*Anal. Chem.* **35** pp 637, 1963)

Physicochemical properties for MTBE, ethanol, benzene and isooctane

Property	Fuel Compound			
	MTBE	Ethanol	Benzene	Isooctane
MW (g/mol)	88.15	46.07	78.11	114.23
Boiling point(°C)	55.2	78.2	80.1	99.2
Density (g/mL)	0.741	0.789	0.879	0.69
K_{ow}	8.71	0.50	135	12,200
Vapor pressure†(kPa)	33.3	7.9	12.6	6.49
Solubility (mg/L)	51,000	Miscible	1,800	2.44
Henry's law† (Pa-m^3/mol)	59.5	0.64	562	323,000

†at 25°C

Air

- **Releases to the atmosphere**
  - **Incomplete combustion and evaporative emissions from vehicles and fuel delivery systems**
  - **Evaporation from direct spills on land and water**
- **Calculated rates of evaporation using two-film model for a pool of pure compound in mol/m^2-h** (Wind speed 1 m/s at 10 m from surface)
  - **MTBE 140**
  - **Benzene 57.6**
  - **Ethanol 43.2**
  - **Isooctane 25.2**
  - **Water 23.0**

Atmospheric reactions

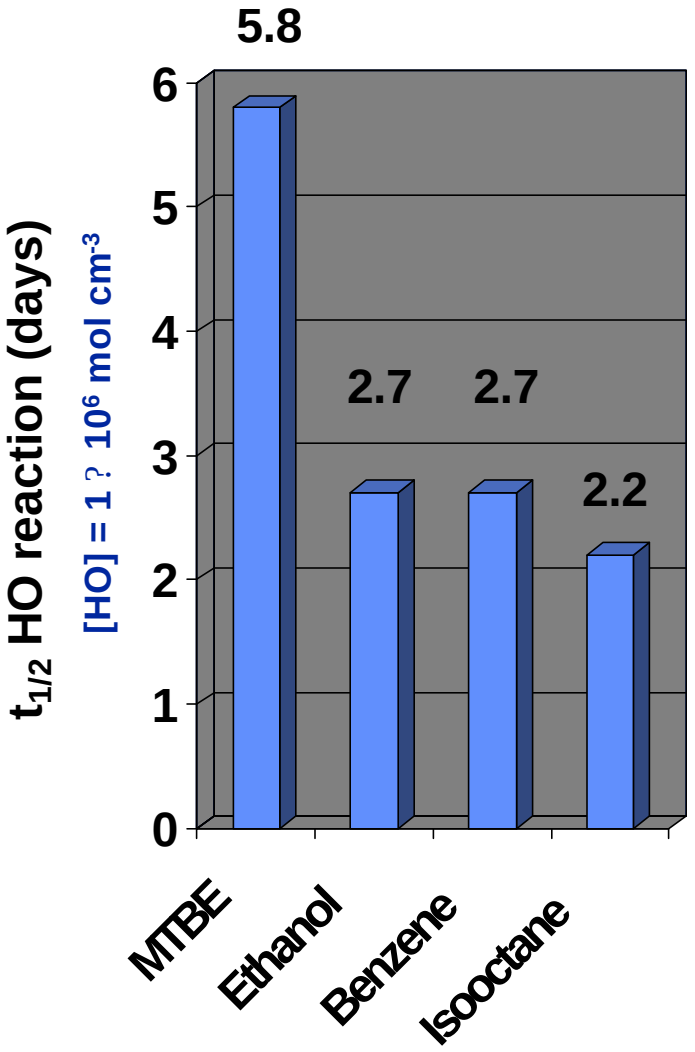
- **Main degradation reaction**

  $HO + RH \rightarrow R^{\cdot} + H_2O$

  - For alkanes with 2 to 8 carbons, $k_{HO} \sim (0.3—9) \times 10^{-12}$ cm^3 mol^{-1} s^{-1}
  - Methane $k_{HO}=0.0084 \times 10^{-12}$ cm^3 mol^{-1} s^{-1}, very long-lived, most abundant in atmosphere

- **Ozone forming potential in the maximum incremental reactivity scale (Carter, 1994)**

	MIR [g O_3/g]
MTBE	0.62
Ethanol	1.34
Benzene	0.42
Isooctane	0.93
Olefins	up to ~10



Water

- **Alkylates solubility in water is very low (10^{-4}—10^{-5} M)**
  - **Ethanol as cosolvent can increase the solubility of alkylates**
    - **E.g.: Calculations show that for an ethanol concentration in water of 10% [v] the solubility of isooctane would increase by ~1.5**
- **Alkylates have high Henry's law constants ↴ in air-water systems they concentrate mainly in the air phase**
  - **The mass transfer velocity based on the two-film model for surface waters is ~0.3 m/day‡, for isooctane, benzene, and MTBE; in contrast, for ethanol, it is ~0.05 m/day ‡**

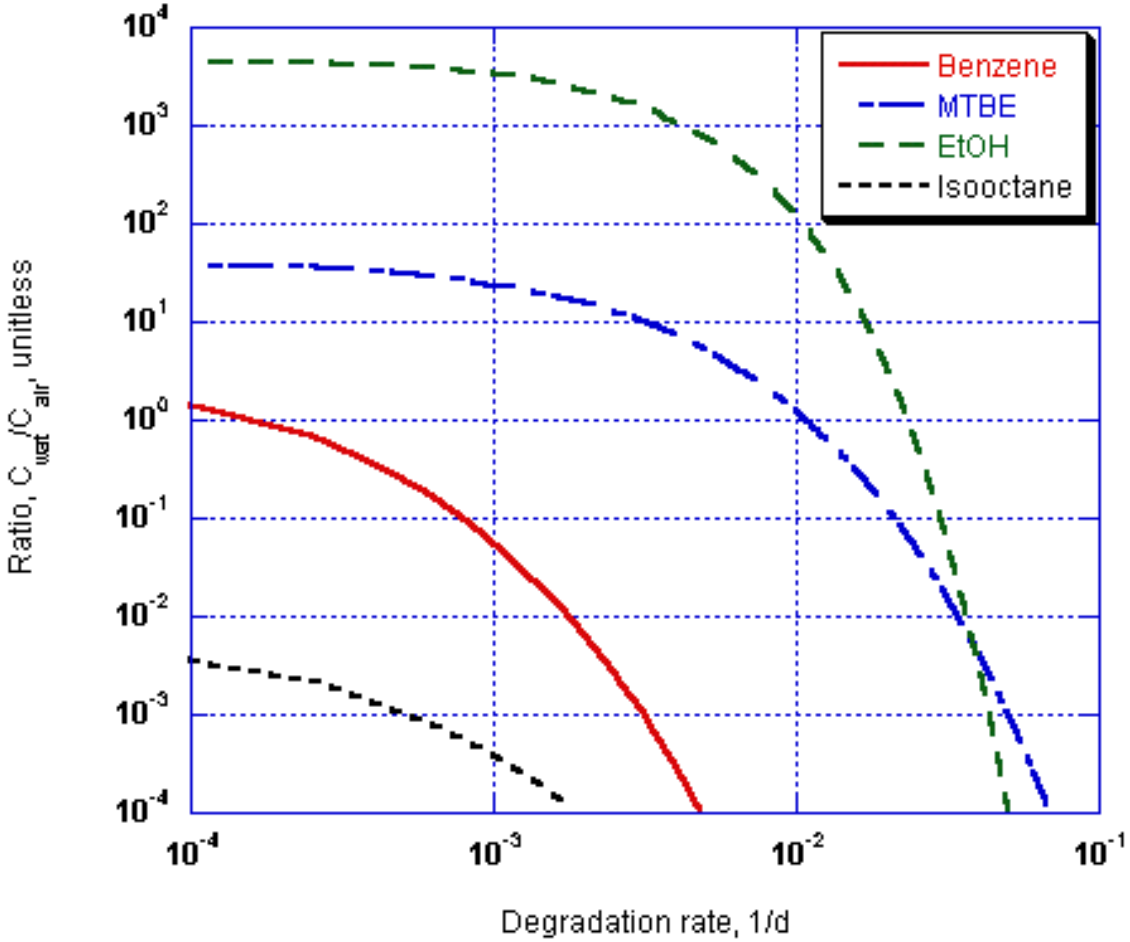
    ‡wind velocity at 10 m from surface = 1 m/s
  - **Rainout calculation**
    - **Calculation of concentration in rain water using a concentration in air of 1 ppb [v] and assuming equilibrium**

Ethanol	**7.33 ? g/L**
MTBE	**0.17 ? g/L**
Isooctane	**0.000036 ? g/L**

Relative impacts of atmospheric rainout of fuel compounds on shallow ground water

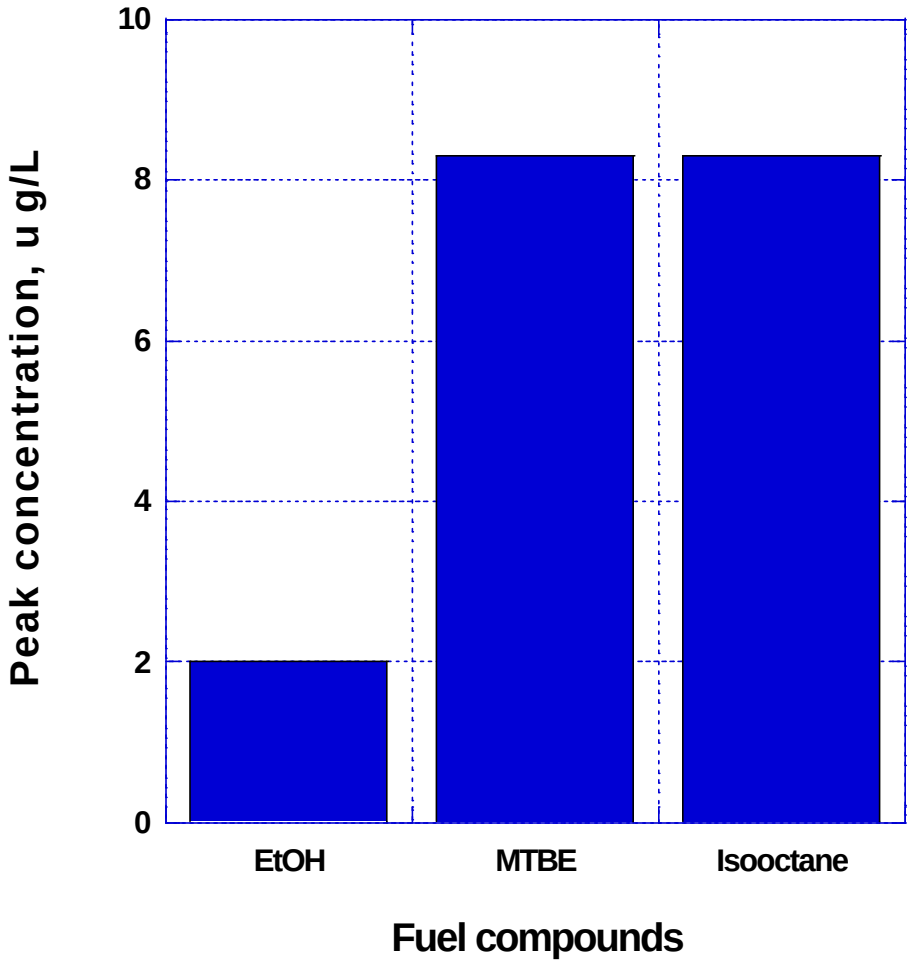
Baehr's model (1999) was used to simulate the impact of rainout onto a sandy soil with a depth of 5 m to the water table

The relative impacts on ground water are described by the ratio of the concentration of a fuel compound in ground water to its concentration in air



Impact to water or soil systems also depends on (bio)degradability, e.g., Predicted concentrations in a lake after a continuous, 7-day release of 40 kg/d

- Reference conditions are an epilimnion of 8 m and an average wind speed of 3 m/s
- With an assumed half-life of 24 hr, ethanol attains a substantially lower concentration in surface water than the other fuel compounds
- The water-to-air mass transfer of both MTBE and isooctane are limited by resistance in the water phase
- The estimated volatilization half-lives for these two compounds are 15-16 days



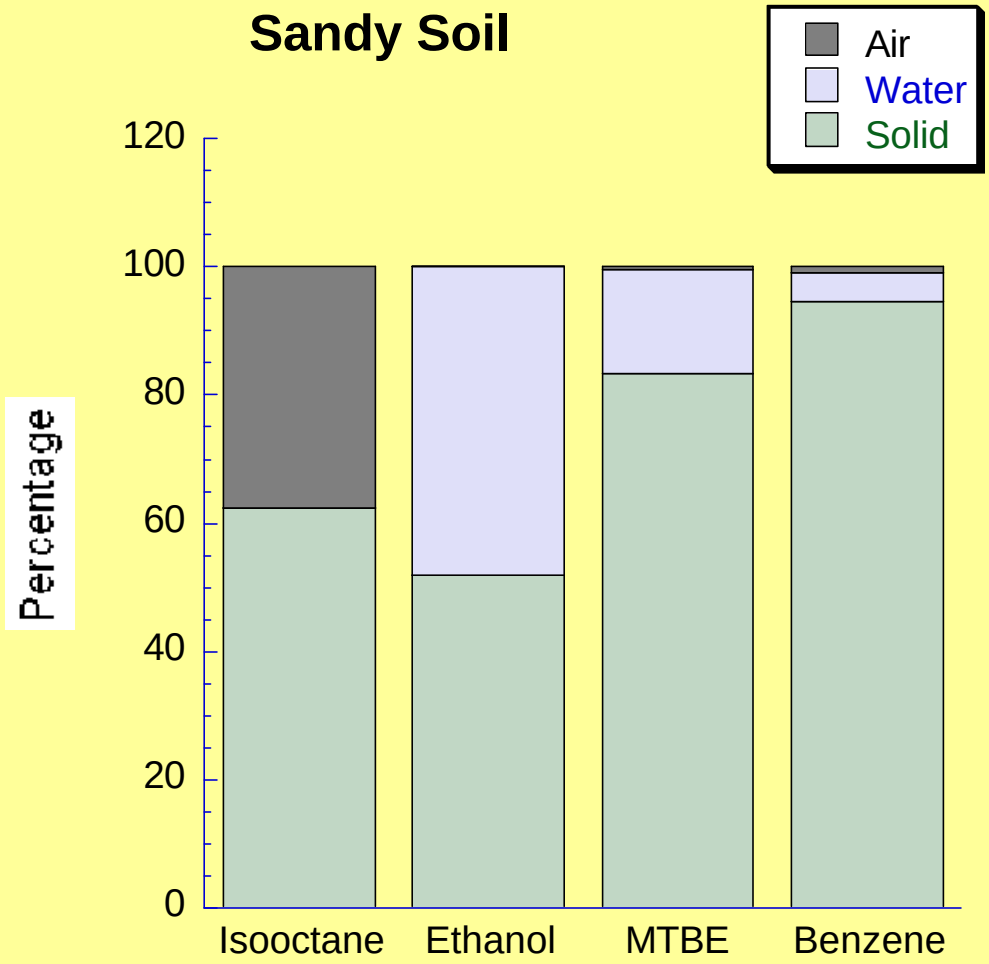
Soils: distribution among phases

Soil Characteristics

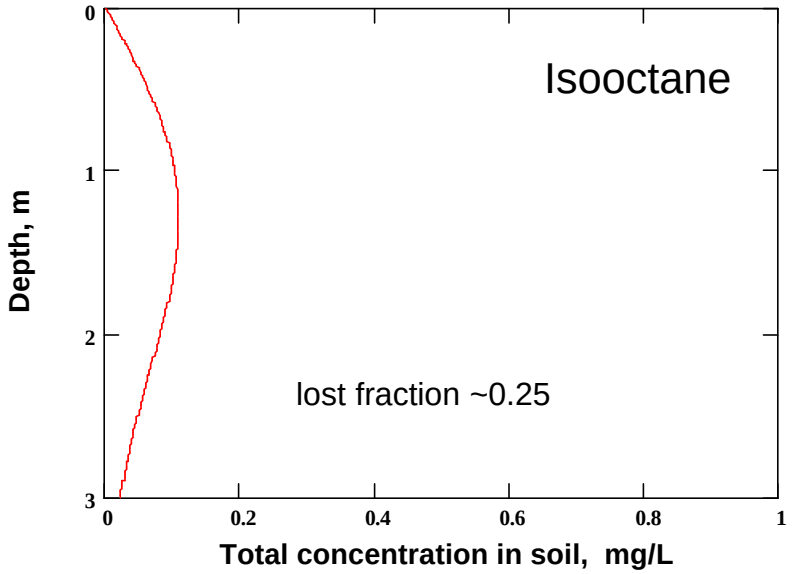
Density	**1.59**	**g/cm³**
Porosity	**0.4**	**L/L**
Water cont.	**0.18**	**L/L**
$f_{organic\text{-}carbon}$	**0.0075**	
Precipitation	**100**	**cm/y**
Infiltration rate	**18**	**cm/y**

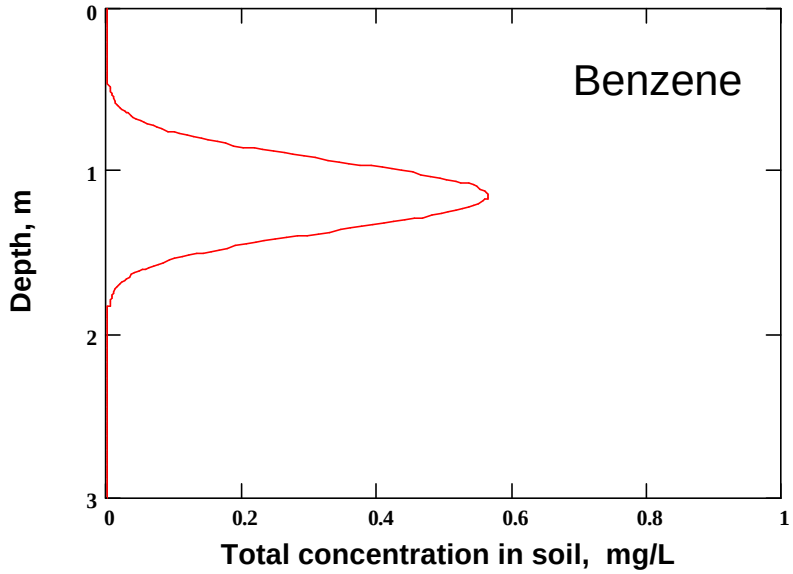
Tranport and losses in soil can be estimated using Jury's model (1990) with corrections by Robinson (2000)

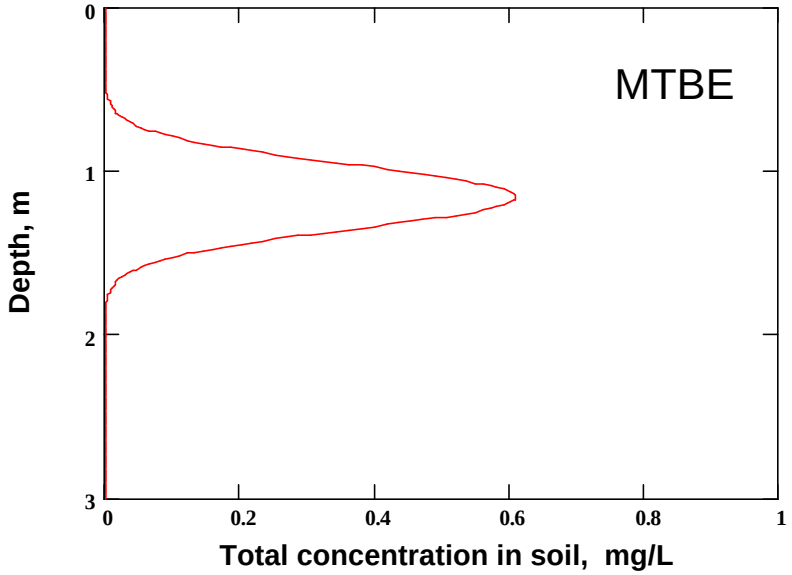
E.g.:
Sandy soil with a buried 1-m deep and 30-cm thick source; source concentration is 1 ppm and concentration in air is zero

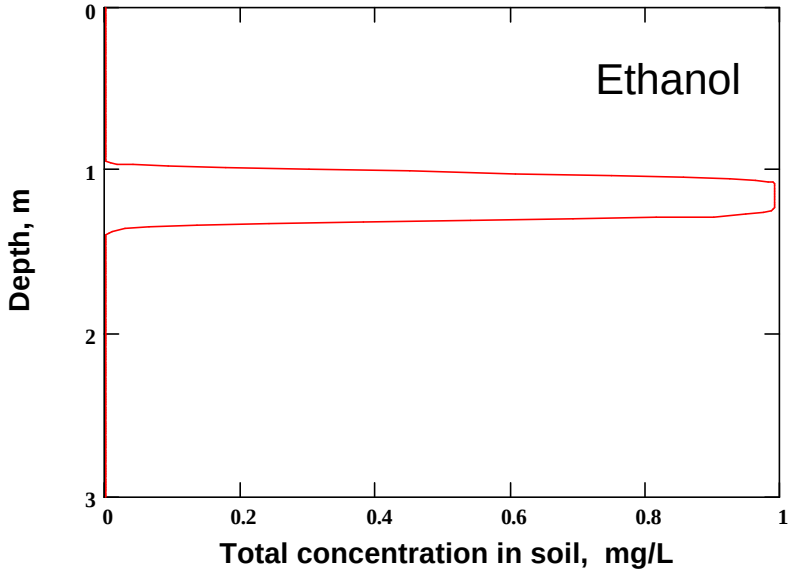


Concentration profiles in soil for a 1 ppm 30-cm wide 1-m deep input pulse after 5 days









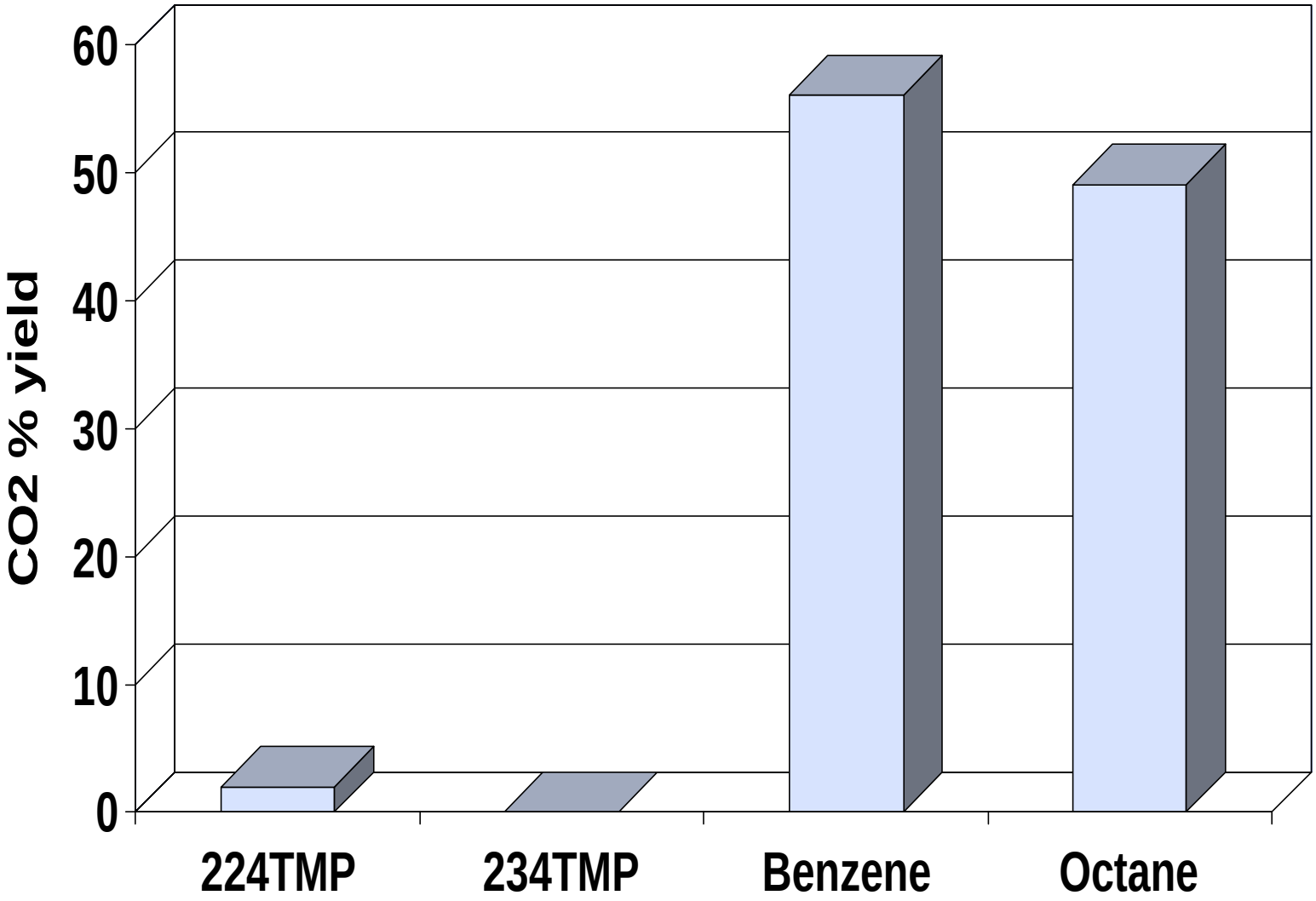
Biodegradation of isooctane

- A laboratory experiment conducted by Solano-Serena (1998) used an unpolluted forest soil to incubate a gasoline solution. After 28 days at 30^{o}C, 20 % of the isooctane was degraded. Benzene, in contrast, was completely degraded

- The corresponding degradation half-life is about 88 days for isooctane

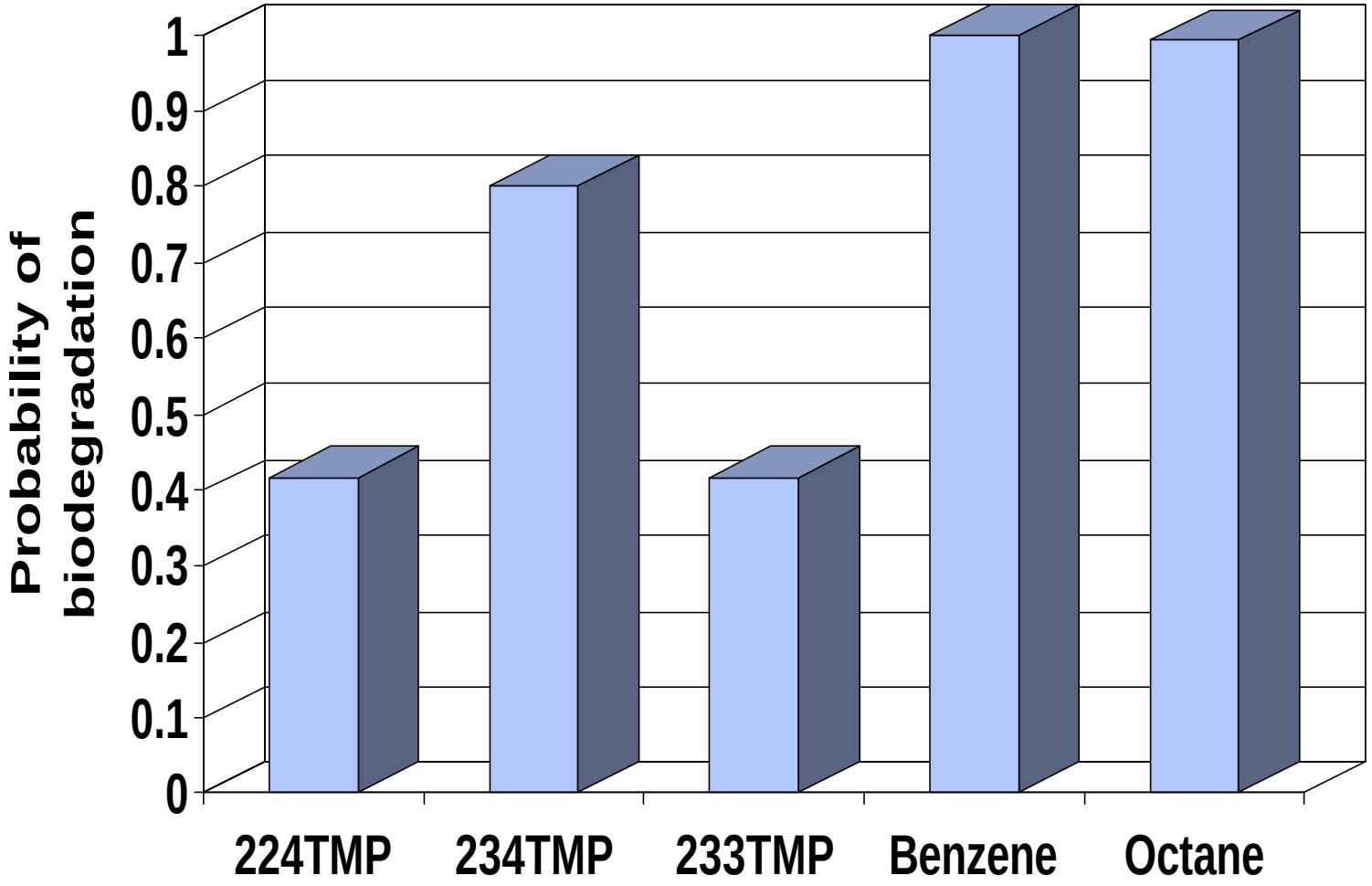
- Based on the results of a field study of a contaminated aquifer by Nielsen (1996), it is likely that the *in-situ* degradation of isooctane will be considerably longer and will depend in part on the occurrence of certain natural microorganisms capable of degrading fuel hydrocarbons

Biodegradation: mineralization yields in unpolluted soil



Mineralization of individual hyrdrocarbons by native soil microflora after 34 days of incubation at 30°C. From Solano-Serena *et al.* (1998)

Biodegradation prediction (BIOWIN)



Probability of biodegradation by group contribution method: program BIOWIN v4.0 from the Syracuse Research Corporation. **Probability > 0.5** implies readily biodegradable

Summary

- Alkylates—mostly branched C8-alkanes
  - Low solubility in water
  - High Henry's law constant
  - Less dense than water
  - High K_{ow}
- Transport and fate in the environment
  - Surface releases
    - Air is the major sink; HO-oxidation with 2-3 days halflife
    - Moderate ozone forming potential compared to other gasoline components
    - Possibly minimal impact on waters
  - Subsurface releases
    - Depending on soil characteristics and source location significant migration to the atmosphere is possible
    - There is also strong absorption in the soil organic phase (high K_{ow})
    - Branched alkanes tend to be recalcitrant—only few experimental biodegradation studies